Application Note

Quantifying the Etch Rate of Borosilicate Glass Exposed to Dishwasher Detergents Using QCM-D

The chemical etching and degradation of borosilicate glass in alkaline media is a critical factor in industrial cleaning and consumer dishwashing. Standard analytical methods, such as gravimetric analysis or ICP-MS, are inherently limited to endpoint data and fail to resolve rapid, transient interfacial kinetics. This application note demonstrates the use of Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) for the real-time, in-situ quantification of these processes using the qCell T system operated via qGraph software. Borosilicate-coated quartz sensors were exposed to alkaline detergent solutions under controlled flow and temperature profiles. QCM-D tracking successfully captured the entire adsorption–induction–etching sequence within a single experiment: initial detergent introduction caused a characteristic frequency drop (Δf) from surfactant adsorption, followed by a continuous frequency increase revealing progress of glass dissolution. Simultaneously, shifts in the resonance bandwidth (ΔΓ or ΔD) resolved distinct phases of surface roughening and smoothing. Utilizing the Sauerbrey relation, quantitative layer thickness changes and temperature-dependent etch rates were rapidly extracted in just a few hours. The results highlight the qCell T, optionally automated via a LiquiBox autosampler, as a powerful tool for rapid detergent formulation screening and material durability testing.

Summary

The etching of borosilicate glass in alkaline aqueous environments is a general corrosion process relevant to a range of applications, including industrial and laboratory cleaning as well as consumer dishwasher operation. In these systems, elevated temperature, strongly alkaline media, and varying organic load defines the chemical environment and determine the rate of glass dissolution. As a result, glass degradation is not only temperature-dependent but can also be influenced by the presence of surface-active species and organic residues introduced during realistic cleaning cycles.

More broadly, understanding the kinetics of glass corrosion requires methods that resolve interfacial processes under liquid-phase conditions over time. Conventional approaches such as gravimetric analysis, chemical quantification of dissolved species (e.g., ICP-OES or ICP-MS), and post-exposure surface characterization typically provide only endpoint information and do not capture transient effects such as initial surface conditioning, temperature-dependent changes in dissolution rate, or concurrent adsorption and material loss.

Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) enables continuous, in situ measurement of

net mass and interfacial property changes at solid–liquid interfaces by tracking shifts in resonance frequency (Δf) and energy dissipation (ΔD or ΔΓ). From the temporal evolution of the frequency signal, effective mass-loss rates can be derived, enabling extraction of temperature-dependent etch kinetics under controlled flow conditions.

In addition, dissipation changes during the etching process provide insight into evolving interfacial properties, which can be related to viscoelastic changes, hydration layer formation, and effective roughness as the glass surface is progressively altered.

In this study, QCM-D measurements are performed in a flow- and temperature-controlled environment using the qCell T. This enables systematic variation of temperature while maintaining constant chemical exposure conditions and allows direct comparison of etch rates across temperatures within a consistent experimental framework.

Data acquisition and experimental control are performed using qGraph, which records real-time frequency and dissipation overtones with scripted control of temperature and pump rate, with optional full automation via integration of the LiquiBox autosampler.

This application note demonstrates the use of QCM-D for quantifying temperature-dependent etch rates of borosilicate glass in alkaline detergent solutions and for resolving concurrent changes in interfacial viscoelastic response during chemical surface degradation.

Samples and Experimental Details

Borosilicate-coated 5 MHz quartz sensors were mounted in a qCell T 5010 temperature-controlled QCM-D flow cell(3T analytik). Experiments were conducted at 20, 40, or 60 °C using deionized water as the baseline fluid. A commercial dishwasher powder was dissolved in water at a fixed concentration of 4 g L^{-1}.

After thermal equilibration, a stable baseline in water was established. Detergent solution was introduced at a constant flow rate of 65 µL min^{-1}. Frequency (Δf) and damping (ΔΓ) were recorded continuously at the 3rd, 5th 7th and 9th overtone (15, 25, 35, 45 MHz, respectively) throughout the following phases: transition from air to water, detergent adsorption, extended exposure to quantify borosilicate etching, and rinsing with baseline fluid.

The frequency response was found to be similar across all overtones (no spreading), confirming that the Sauerbrey relation applies as expected due to the rigid nature of borosilicate glass. Further analysis was therefore limited to the third overtone alone.

Etch rates were determined from the linear slope of the frequency increase during the etching phase. Since borosilicate glass is a rigid coating, the Sauerbrey relation was applied to convert frequency shifts to mass per unit area:

$$\Delta\varphi = -C_f \cdot \Delta f$$

where C_f=17.8 ng·cm^{-2}·Hz^{-1} is the sensitivity coefficient for a 5 MHz crystal and $\Delta\varphi = \Delta m / A_q$ represents the surface mass density. Layer thicknesses were calculated by dividing Δφ by the borosilicate density (ρ =2.23 g cm^{-3}).

For these analyses, dedicated software modules were used to convert frequency into mass per unit area and to calculate layer thickness. These modules are available within the qGraph viewer data post-processing software.

Results

Frequency Response and Etch Rate

Figure 1 shows the QCM-D frequency response for 3rd overtone during detergent exposure and borosilicate etching at 20 °C. Frequency is referenced to the baseline fluid and begins at zero. Detergent adsorption produces a gradual decrease of ~25 Hz over 50 minutes. After approximately 70 minutes, the frequency begins to increase linearly, defining the induction time for etching. The slope of this increase determines the etch rate. At 120 minutes, replacement with DI water induces a rapid frequency increase due to the removal of detergent from the surface and reduced viscosity. The final baseline offset represents the net mass loss.

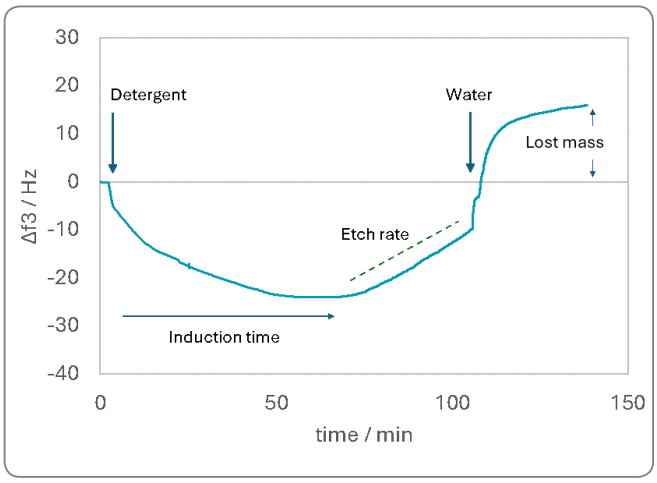

Figure 1. Frequency shift at 20 °C with annotated indicators: detergent introduction, induction time, etch slope, and baseline offset.

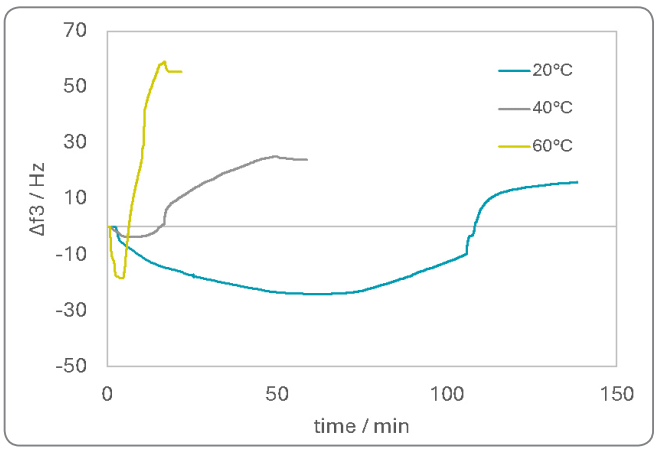

Figure 2. Frequency shift of the 3rd overtone (15 MHz) at 20, 40, and 60 °C showing temperature-dependent etching behavior.

Figure 2 compares frequency responses of the 3rd overtone (15 MHz) at 20, 40, and 60 °C. Elevated temperatures reduce the induction time and accelerate etching, while total mass loss (baseline offset) increases despite shorter exposure times.
Extracted etch data are summarized in Table 1. The observed temperature dependence is consistent with thermally activated glass dissolution.

Table 1. Etch data from frequency curves

Temperature	Exposure time	Induction time	Etch rate (nm/h)	Thickness change (nm)
20 °C	105 min	63 min	2.1	1.3
40 °C	50 min	6.75 min	5.6	1.9
60 °C	15 min	2.25 min	17.0	4.4

While frequency reveals the etching-induced borosilicate mass loss, damping (ΔΓ) provides complementary information on surface morphology. In classical QCM-D interpretation for viscoelastic layers, damping arises from dissipative energy losses due to mechanical deformation of the adsorbed layer under oscillation. This results in friction between molecules within the layer, whereby some of the vibrational energy converts to heat.
For rigid materials like borosilicate glass, there is minimal – if any – mechanical deformation of the layer as such, yet damping still provides valuable insight. Here, damping originates primarily from hydrodynamic interactions between the oscillating crystal and the surrounding liquid. The energy dissipates because of deformation of the liquid, not the layer itself. Surface roughness or pitting increases the effective contact area with the fluid, which enhances energy dissipation, whereas smoothing of the surface reduces hydrodynamic coupling and thereby damping (1). This contrast clearly demonstrates that damping is not only relevant for soft, viscoelastic films but can also report on the topography and morphology of rigid surfaces (figure 3).

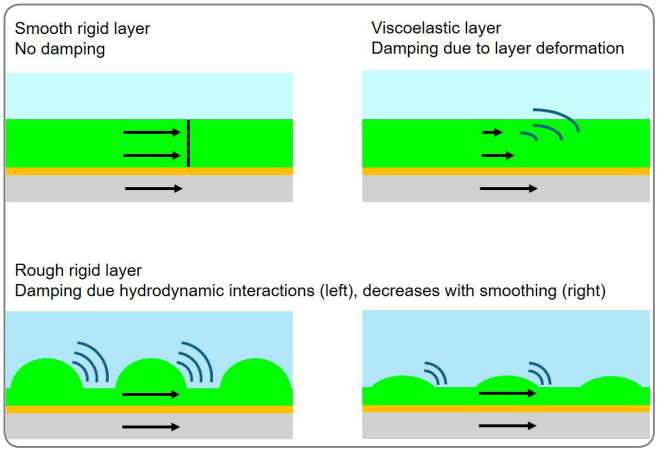

Figure 3. Shematic illustration of mechanism for dissipative energy losses in comparison to a smooth rigid layer (top left). Viscoelastic layers dissipate energy through mechanical deformation (top right) while rough rigid layers dissipate energy through hydrodynamic interactions (lower left). The hydrodynamic influence on energy dissipation is lowered as the rough rigid surface is smoothened (lower right).

Figure 4 shows damping signals during detergent exposure and etching. At 40 and 60 °C, damping rises sharply in the early stages due to pitting and roughening, then levels off and decreases as the surface smoothens. At 20 °C, damping increases continuously, indicating that 120 minutes of exposure was insufficient to reach the smoothing regime observed at higher temperatures.

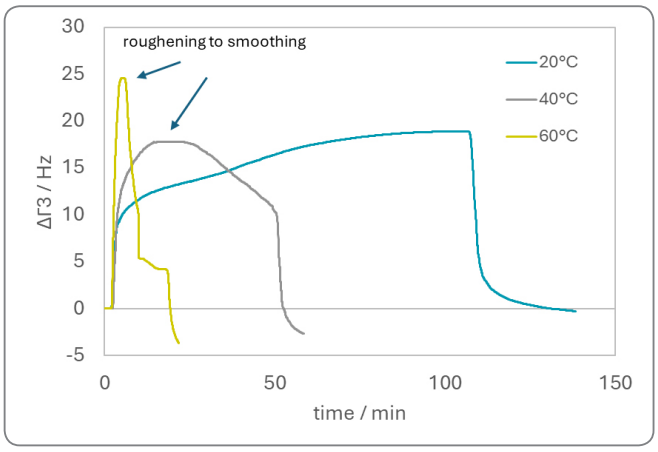

Figure 4. Damping shifts at 20, 40 and 60 °C showing temperature dependent etching behaviour.

Conclusion

This application note demonstrates that QCM-D can be used to quantify borosilicate glass etching under controlled detergent exposure in real time. Key insights include:

- Temperature-dependent induction time and etch rate
- Surface roughening and smoothing dynamics revealed via damping
- Quantitative layer thickness estimation using the Sauerbrey relation
- Rapid acquisition of etching kinetics, enabling full experiments and analysis in just a few hours

By combining high sensitivity, real-time measurement, and multiparameter analysis, QCM-D provides a powerful tool for studying detergent–glass interactions, formulation effects, and material durability, delivering results much faster than conventional offline methods.

Reference

(1) I Reviakine, D Johannsmann, RP Richter; Hearing what you cannot see and visualizing what you hear: interpreting quartz crystal microbalance data from solvated interfaces; Analytical chemistry 83 (23), 8838-8848

Experimental Hardware: qCell T Q2 eChem

Borosilicate glass etching data were acquired using the high-sensitivity qCell T Q2 eChem platform, a dual-channel QCM-D instrument based on the qCell T 5O10 architecture. This platform provides the precise dynamic temperature control 4-65 °C and software-controlled fluidics essential for tracking kinetic etch-rates during chemical degradation. For expanded workflows, the system can be integrated with a Liquibox compact auto-sampling unit for automated fluid handling of up to 8 samples per channel. Additionally, its dual-channel architecture offers full compatibility with electrochemical modules, enabling correlated tracking of real-time mass changes and viscoelastic properties alongside electrochemical interface processes.

The instrument features a quick-release flow cell sealed via a bayonet-locking mechanism. Equipped with dedicated quartz positioning adaptors, the flow cell accommodates various quartz sensor geometries with fundamental frequencies of either 5 MHz or 10MHz. While 10 MHz sensors offer higher mass sensitivity 4.3 ng $cm^{-2}Hz^{-1}$ vs. 17.8 ng $cm^{-2}Hz^{-1}$ for 5MHz, 5MHz sensors allow probing of more harmonics (1st, 3rd, 5th, 7th, and 9th), which provides an advantage for QCM-D data modeling. In a dual-channel configuration, both sensor types can be operated in parallel within the instrument's 1–50 MHz frequency range to collect a total of 8 combined harmonics. For this study, 5MHz quartz sensors were selected.

Data post-processing was performed via the qGraph viewer software. In this study, dedicated modules were used to convert frequency shifts into mass per unit area and calculate layer thickness. For broader application workflows, the software additionally features advanced modules for electrochemical data synchronization, kinetic modeling, and discrete particle analysis.

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